Oxidation of Organic Substrates catalysed by *trans*-$[Ru^{III}(phen)_2(OH)(OH_2)][ClO_4]_2$ and *trans*-$[Ru^{III}(bpy)_2(OH)(OH_2)][ClO_4]_2$ (phen = 1,10-Phenanthroline; bpy = 2,2′-Bipyridine)

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trans-$[Ru^{III}(phen)_2(OH)(OH_2)][ClO_4]_2$ and *trans*-$[Ru^{III}(bpy)_2(OH)(OH_2)][ClO_4]_2$ (bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline) are active catalysts for the PhIO and aerobic oxidation of organic substrates; a modified electrode, through adsorption of *trans*-$[Ru^{III}(phen)_2(OH)(OH_2)][ClO_4]_2$, was active in the oxidation of alcohol to give aldehyde (or ketone).

The oxidation of organic substrates catalysed by transition metal complexes represents an important area in homogeneous catalysis.[1] It is well-known that metal complexes containing extensive π-unsaturated ligand adsorb easily and irreversibly on pyrolytic graphite electrode[2] and that high-valent oxo complexes of ruthenium containing π-aromatic amines such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) are active oxidants.[3] We thus became interested in the chemistry of *trans*-$[Ru^{III}(phen)_2(OH)(OH_2)][ClO_4]_2$ (**1**)[3] and *trans*-$[Ru^{III}(bpy)_2(OH)(OH_2)][ClO_4]_2$ (**2**),[4] since their high-valent oxo derivatives, generated by chemical or electrochemical means, are potent oxidants of organic substrates. We describe here some aspects of complexes (**1**) and (**2**) and their role in the chemical, electrochemical, and catalytic aerobic oxidation of organic substrates.

trans-$[Ru^{III}(L)_2(OH)(OH)_2][ClO_4]_2$
(**1**) L = phen
(**2**) L = bpy

The cyclic voltammogram (c.v.) of (**1**) at pH = 1.1 (Figure 1) is similar to that of (**2**) (or *trans*-$[Ru^{VI}(bpy)_2O_2][ClO_4]_2$) with three well-defined couples [potentials in V *vs.* normal hydrogen electrode (n.h.e.)] (I)—(III).

$$trans\text{-}[Ru^{III}(phen)_2(OH)(OH_2)]^{2+} + e + H^+ \rightarrow trans\text{-}[Ru^{II}(phen)_2(OH_2)_2]^{2+},\ E_{\frac{1}{2}} = 0.80 \quad (I)$$

$$trans\text{-}[Ru^{IV}(phen)_2(O)(OH_2)]^{2+} + e + H^+ \rightarrow trans\text{-}[Ru^{III}(phen)_2(OH)(OH_2)]^{2+},\ E_{\frac{1}{2}} = 1.01 \quad (II)$$

$$trans\text{-}[Ru^{VI}(phen)_2O_2]^{2+} + 2e + 2H^+ \rightarrow trans\text{-}[Ru^{IV}(phen)_2(O)(OH_2)]^{2+},\ E_{\frac{1}{2}} = 1.30 \quad (III)$$

As expected, ΔE_p (peak-to-peak separation) for couple (III) is ~30 mV at a slow scan rate (<100 mV s^{-1}) and $E_{\frac{1}{2}}$ *vs.* pH (pH = 1—4) showed a linear plot with slope of −60

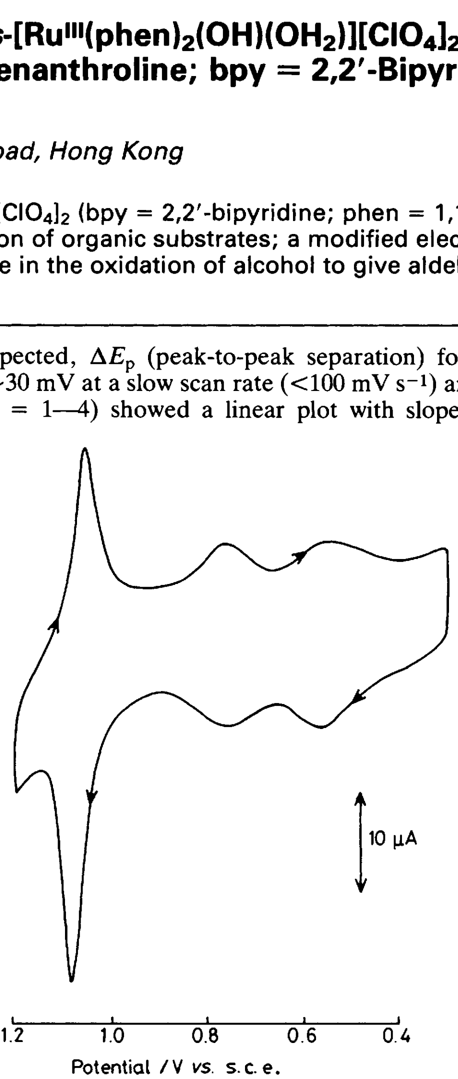

Figure 1. Cyclic voltammogram of *trans*-$[Ru^{III}(phen)_2(OH)(OH_2)][ClO_4]_2$ (**1**) (~0.5 mM) in 0.1 M CF_3CO_2H (pH = 1.1). Working electrode, pyrolytic graphite; scan rate, 50 mV s^{-1}.

Table 1. Oxidation of organic substrates with PhIO catalysed by some ruthenium(III) complexes.

Catalyst	Substrate	Products (% yield)	Solvent	% Yield[a]	Turnover number, reaction time/h
(**1**)	Cyclohexene	Cyclohexene oxide (38.7), cyclohex-2-enone (14.6)	Acetone	53.3	147, 3½
(**2**)	Cyclohexene	Cyclohexene oxide (44.4), cyclohex-2-enone (9.3)	Acetone	53.7	165, 4½
$Ru^{III}(OEP)(PPh_3)Br$[b]	Norbornene	Norbornene oxide	CH_2Cl_2	8	4, 6
(**2**)	Norbornene	Norbornene oxide	Acetone	26	15, 6
(**2**)	Styrene	Styrene oxide	Acetone	3.4	5.5, 6

[a] Based on PhIO used, this does not include loss of PhIO owing to its self-decomposition to PhI. [b] Ref. 8. OEP = octaethylporphinato.

mV/pH unit in accord with a two-proton two-electron transfer process. *trans*-$[Ru^{VI}(phen)_2O_2][ClO_4]_2$ has also been isolated by Ce^{IV} oxidation of complex (**1**) in water. It is a diamagnetic yellow solid and exhibits an intense i.r. band at ~850 cm^{-1} characteristic of the $\nu_{asym.}(RuO_2)$ stretch in Ru^{VI}-dioxo species.[5] The $E_{\frac{1}{2}}$ values of the Ru^{VI}/Ru^{IV} couple of *trans*-$[Ru^{VI}(phen)_2O_2]^{2+}$ (1.30 V) and *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ (1.25 V)[5] are similar. The cyclic voltammogram of (**1**) (~1 mM) in 0.1 M CF_3CO_2H in the presence of propan-2-ol (1 M) indicated the presence of a catalytic oxidation current [approximately four times as large as the i_{pa} of couple (III)] found beyond the Ru^{IV}/Ru^{III} couple. Controlled potential electrolysis of this solution at 1.05 V *vs*. n.h.e. produced acetone with over 85% current efficiency (turnover number 15). No other organic product was formed. However, if the electrolysis was carried out at 1.25 V, both the current efficiency† and catalytic activity of the ruthenium complex decreased. At this stage, the optical spectrum of the solution resembled closely that of $[(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2]^{4+}$,[6] but its cyclic voltammogram was complex. With reference to Meyer's work on *cis*- and *trans*-$[Os(bpy)_2O_2]^{2+}$,[7] it is likely that some bpy ligand became dissociated from the metal ion. Similar results have also been found for (**2**).

An important feature in which (**1**) is distinctly different from (**2**) is its ease of adsorption on edge plane pyrolytic graphite electrode. The modified electrode was fabricated by cycling the pyrolytic graphite electrode between 1.25 and 1.0 V in a 0.1 M CF_3CO_2H solution of (**1**) (0.5 mM) for 15 minutes. The resulting electrode was then rinsed with deionized water; its cyclic voltammogram in 0.1 M CF_3CO_2H solution is shown in Figure 2(a). Figures 1 and 2(a) are similar in shape indicating that the adsorbed complex remained in the same chemical form as *trans*-$[Ru^{III}(phen)_2(OH)(OH_2)][ClO_4]_2$. The amount of complex adsorbed was estimated to be 10^{-10} mol cm^{-2}.‡ Further experiments indicated that the pH of the solution (pH <7) has little effect on the adsorption. Importantly, this modified electrode is capable of oxidizing propan-2-ol to acetone at potential ~1.2 V *vs*. n.h.e. [Figure 2(b)].

The oxidation of cyclohexene and norbornene by PhIO is catalysed by (**1**) or (**2**). Table 1 summarizes the results of these oxidative reactions. In a typical experiment, (**2**) or (**1**) (2 mg), PhIO (200 mg), and cyclohexene (1 ml)/norbornene (100 mg) /styrene (1 ml) were stirred in acetone (2 ml). The organic products, cyclohexenone, cyclohexene oxide, *exo*-norbornene oxide, and styrene oxide were identified by g.c.–mass spectrometry. As shown in Table 1, complexes (**1**) and (**2**) are much better catalysts than $Ru^{III}(OEP)(PPh_3)Br$.[8] *trans*-$[Ru^{VI}(phen)_2O_2][ClO_4]_2$ and *trans*-$[Ru^{VI}(bpy)_2O_2][ClO_4]_2$ were found not to react with a C=C double bond[9] indicating that they are not the reactive intermediates. It is likely that a Ru^V=O (or Ru^{IV}=O) intermediate generated *in situ* may be responsible for the observed epoxidation. We note that addition of PhIO to an acetone solution of (**1**) or (**2**) produced a species having a similar optical spectrum to *trans*-$[Ru^{IV}(bpy)_2O(OH_2)]^{2+}$.[5]

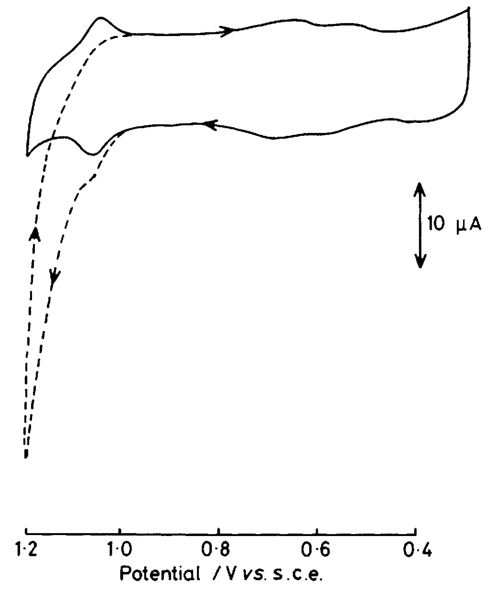

Figure 2. Cyclic voltammogram of the modified pyrolytic graphite electrode (see text) in (a) 0.1 M CF_3CO_2H (——) and (b) 0.1 M CF_3CO_2H + 1 M propan-2-ol (---); scan rate, 50 mV s^{-1}.

Stirring complex (**1**) (4 mg) with benzyl alcohol (1 ml) (or norbornene (90 mg)) in acetone (2 ml) saturated with air for 2—3 days at 25 °C resulted in the catalytic aerobic oxidative reaction. The organic product, benzaldehyde (or *exo*-norbornene oxide), was found with a turnover number (based on the amount of metal complexes used) of 4—5. Under degassed conditions, no reaction was found between (**1**) and norbornene. Importantly, the Ru complex remained intact (judging from the optical spectrum) after the oxidative reactions. Even though the turnover number is low, this result does indicate the potential uses of Ru^{III}-OH complexes in aerobic oxidative

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† Repeated experiments indicated that the current efficiency could be as low as 50% after a turnover of 20. The low current efficiency could be attributed to the degradative oxidative side reactions of the ruthenium catalyst and the solvent decomposition reaction.

‡ Total amount of complex adsorbed was calculated by integrating the peak area in the c.v. scan (~ 3 × 10^{-11} mole); the electrode surface area, as determined by rotating disc voltammetric technique, was 0.30 cm^2.

reactions. The open co-ordination sites in (**1**)/(**2**) makes this an attractive system in the study of dioxygen uptake reaction.

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